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(54) LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a negative electrode active material suppressed for collapse and having a high capacity and a long life by forming the negative active material bearing the charging/discharging of a negative electrode material with grains containing the phase storing lithium and the phase storing no lithium.

SOLUTION: In a negative electrode material, the phase-storing lithium is made of one of 3B, 4B, 5B group elements, and it is preferably made of one of Al, Ga, In, Si, Ge, Sn, Pb, Sb, Bi. The phase-storing lithium is the phase of an inter-metallic compound made of at least one kind of element among Al, Ga, In, Si, Ge, Sn, Pb, Sb, Bi. The phase which stores no lithium is preferably a phase made of one of 4A, 5A, 6A group elements and at least one kind of element from among Mn, Fe, Co, Ni, Cu.

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CLAIMS

[Claim(s)]

[Claim 1] The negative-electrode ingredient for lithium secondary batteries characterized by consisting of particles containing both the phase to which the negative-electrode active material which bears the charge and discharge of said negative-electrode ingredient for a lithium ion in occlusion and the negative-electrode ingredient for lithium secondary batteries to emit at the time of charge and discharge can carry out occlusion of the lithium, and the phase which does not carry out occlusion of the lithium.

[Claim 2] The negative-electrode ingredient for lithium secondary batteries characterized by the phase which can carry out occlusion of the lithium for a lithium ion in occlusion and the negative-electrode ingredient for lithium secondary batteries to emit at the time of charge and discharge according to claim 2 being a phase which consists of 3B, 4B, or 5B group element.

[Claim 3] The negative-electrode ingredient for lithium secondary batteries characterized by the phase which can carry out occlusion of the lithium for a lithium ion in occlusion and the negative-electrode ingredient for lithium secondary batteries to emit at the time of charge and discharge according to claim 2 being a phase which consists of aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, or Bi.

[Claim 4] The negative-electrode ingredient for lithium secondary batteries characterized by the phase which can carry out occlusion of the lithium for a lithium ion in occlusion and the negative-electrode ingredient for lithium secondary batteries to emit at the time of charge and discharge according to claim 2 being a phase of the intermetallic compound which sets at least one kind to one of the configuration elements among aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, and Bi.

[Claim 5] The negative-electrode ingredient for lithium secondary batteries characterized by the phase which does not carry out occlusion of the lithium for a lithium ion in occlusion and the negative-electrode ingredient for lithium secondary batteries to emit at the time of charge and discharge according to claim 2 being a phase which consists of 4A, 5A, a 6A group element, and at least one kind of element of Mn, Fe, Co, nickel, and Cu.

[Claim 6] The lithium secondary battery with which the negative-electrode ingredient of said lithium secondary battery is characterized by being one negative-electrode ingredient of the publications at claims 1-6 in the lithium secondary battery which consists of the negative electrode which makes a lithium ion occlusion and makes a subject the negative-electrode active material to emit, a positive electrode, and the nonaqueous electrolyte or polymer electrolyte of lithium ion conductivity at the time of charge and discharge.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] With respect to a nonaqueous electrolyte rechargeable battery, it has the high voltage, a high energy consistency, high charge-and-discharge capacity, and the charge-and-discharge property of a long cycle life especially, and this invention relates to a lithium secondary battery with high safety.

[0002]

[Description of the Prior Art] In the field of electronic equipment, small lightweight-ization of a device is progressing with the rise of the request which carries out pocket use of the device. For this reason, development of a cell with a high energy consistency, especially a rechargeable battery is demanded. There is a lithium secondary battery as a candidate of the rechargeable battery which fills this demand. Compared with a nickel KADONIUMU cell, a lead accumulator, and a nickel hydride battery, a lithium secondary battery has a high voltage and a high energy consistency, and, moreover, is lightweight.

[0003] However, in order for a lithium to carry out a dendrite deposit on a negative-electrode front face at the time of charge and to carry out negative activation to an internal short circuit and the electrolytic solution with a positive electrode at it in the lithium secondary battery using the lithium metal as a negative-electrode active material, it is a problem in respect of the life of a cell, or safety. Moreover, in order to avoid the danger of using a lithium metal, the lithium secondary battery which used lithium alloys, such as Li-Pb and Li-aluminum, for the negative-electrode active material is developed. However, in this lithium secondary battery, there is a problem of a dendrite deposit or pulverization and sufficient battery life has not been acquired.

[0004] In current, the lithium secondary battery which used the graphite for the negative-electrode active material is developed, and it has resulted in utilization. the reaction from which this inserts a lithium ion between C sides of a graphite, and it is made to secede -- a lithium ion -- occlusion -- if it is emitting and compares with an activity metal lithium chemically, it will be stable and there will also be no dendrite deposit of a lithium. For this reason, the cycle life also became long and safety also improved.

[0005]

[Problem(s) to be Solved by the Invention] When a graphite is used for a negative-electrode active material, it is the discharge capacity of about 300 mAh/g. Since the weight density of a graphite is 2.2 g/cm³, a volume capacity consistency is small compared with a lithium metal, and a volume capacity consistency becomes small further with the negative-electrode sheet which applied the graphite negative-electrode active material to the negative-electrode charge collector. In order to solve this problem, it is effective to use the big metal system inorganic material of weight density for a negative-electrode active material.

[0006] JP,8-124568,A is the rechargeable battery which used for the negative electrode the metal powder which alloyed at least one kind of metal chosen from aluminum, Zn, Sn, and Pb, and at least one kind of metal chosen from nickel, Co, Cu, Ti, and Fe. Since specific surface area of the above-mentioned alloy can be enlarged by etching aluminum, Zn, Sn, and Pb alternatively with an acid or an alkali solution, a touch area with the electrolytic solution increases and it is supposed that diffusion of the lithium ion to a negative electrode can be made easy. Moreover, it is supposed that the dendritic growth of a lithium can be controlled to coincidence. However, since it stops being able to carry out occlusion of the Li to the interior of an ingredient when aluminum, Zn, Sn, and Pb which can carry out occlusion of the Li are alloyed with nickel, Co, Cu, Ti, and Fe which cannot carry out occlusion of the Li, a role of a negative-electrode ingredient is not played substantially.

[0007] In JP,8-255610,A, destruction of the negative electrode by the expansion contraction accompanying the repeat of charge and discharge can be controlled compared with a lithium and the negative electrode which consisted of only metals which form an alloy by using the clad plate of the metal which cannot form easily a lithium, the metal which forms an alloy, a lithium, and an alloy as a negative electrode. Thereby, decline in charge-and-discharge effectiveness is suppressed, and it is supposed that a long lasting lithium secondary battery will be realizable by the high energy consistency. However, it is impossible for the metal layer which forms Li and an alloy in the case of the above clad plates to repeat expansion contraction in connection with charge and discharge, to be unable to avoid destruction, since stress is generated between one Li and the metal layer which does not form an alloy, but to actually use as a negative-electrode ingredient.

[0008] Then, by controlling collapse of the negative-electrode active material by the repeat of charge and discharge, and using this negative-electrode active material, while it is long lasting and offering high capacity, the capacity by the difference in a charge-and-discharge rate, and the negative-electrode active material for lithium secondary batteries with little degradation of a life, charge-and-discharge capacity is large, an energy density is high, and this invention aims at offering the long lithium secondary battery of a cycle life.

[0009]

[Means for Solving the Problem] Artificers came to invent the negative-electrode ingredient for lithium secondary batteries and a lithium secondary battery with a header and the outstanding property for the approach of controlling collapse of a metal system negative-electrode ingredient paying attention to the cause of degradation of a metal system negative-electrode ingredient being in collapse of the structural change generated in the case of charge and discharge, i.e., a negative-electrode ingredient.

[0010] When Li is used into occlusion and Si particle which can be emitted is used as a negative-electrode active material by charge and discharge, as a result of irreversible capacity's producing about 75% and the very large powder which made the particle of Si and Cu compound-ize with a powder sintering process although a charge-and-discharge cycle property is also remarkable and it is bad and carrying

out the same charge and discharge test, irreversible capacity became about 20% and the charge-and-discharge cycle property has also been improved. It found out that the charge-and-discharge property was improved remarkably by consisting of particles in which the negative-electrode active material which bears the charge and discharge of said negative-electrode ingredient for a lithium ion in occlusion and the negative-electrode ingredient for lithium secondary batteries to emit at the time of charge and discharge contains two or more phases on an ingredient organization from this. Since Si particle collapses by charge and discharge and it stops contributing to charge and discharge when the particle is formed by the Si independent, it is thought that a charge-and-discharge property deteriorates.

[0011] By the particle which compound-izes Si and Cu and consists of two phases on the other hand, when Cu which does not contribute to charge and discharge substantially has combined with Si, collapse of Si phase by charge and discharge is controlled, and it is thought that the charge-and-discharge property has been improved. Therefore, the lithium secondary battery which is excellent in a charge-and-discharge property can be offered by using for a negative-electrode ingredient the particle which consists of the phase which does not contribute to charge and discharge like Cu, and the phase which bears charge and discharge like Si. Occlusion and the element which can be emitted belong Li to 3B, 4B, and 5B by charge and discharge like Si, and they are aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, and Bi. The charge-and-discharge property of a lithium secondary battery improves by leaps and bounds by using aluminum, Si, Sn, and Pb especially. Moreover, if the element which can carry out occlusion of these Li(s) is within the limits by which the occlusion property is held even when the unescapable impurity element contains, it will not become the cause of degrading a charge-and-discharge property. Therefore, even when a different element is added, in charge and discharge, it is satisfactory.

[0012] Not only the above-mentioned metallic element simple substance but a certain kind of intermetallic compound is possible for the occlusion of Li, and emission. The intermetallic compound is an intermetallic compound which mainly sets at least one kind in aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, and Bi to one of the configuration elements. These intermetallic compounds have a short cycle life, although charge-and-discharge capacity is large, and it cannot put in practical use only in the very thing. Then, it tried making it compound-ize with the metal which cannot carry out occlusion of the Li. It is NiSi₂ as an intermetallic compound. It used. Although this particle has the initial discharge capacity exceeding 400 mAh/g, its charge-and-discharge life is short. Then, it compound-izes with Cu with a powder sintering process, and is NiSi₂. The particle with two phases of Cu was produced.

[0013] When the charge and discharge test was carried out using this particle, although capacity fell to 350 or less mAh/g, the charge-and-discharge life became long. That is, the charge-and-discharge property has been improved by compound-ization with Cu. Although the discharge capacity of a graphite system negative-electrode ingredient is about 300 mAh/g, a substantial volume capacity consistency since weight density was twice [more than] the graphite, when, as for NiSi₂, it forms a negative-electrode sheet is measured against a graphite system negative-electrode ingredient, and it is 1.5. It is more than twice. Therefore, the charge-and-discharge property improves by compound-izing the intermetallic compound which sets at least one kind in aluminum, Ga, In, Si, germanium, Sn, Pb, Sb, and Bi to one of the configuration elements with the metal which does not carry out occlusion of the Li.

[0014] The metals which do not carry out occlusion of the Li are the metallic element which mainly belongs to 4A, 5A, and 6A group, and Mn, Fe, Co, nickel and Cu. Even if these metals impress a charge and discharge current, they do not carry out occlusion of the Li to the interior. Therefore, there is no expansion contraction accompanying the occlusion of Li and emission also in the case of charge and discharge, and the structure does not collapse. If these metals are compound-ized with the metal which can carry out occlusion of the above Li, the structure is stabilized and degradation of a charge-and-discharge property can be suppressed.

[0015] If the particle with which the phase which can carry out occlusion of the Li especially, and the phase which does not carry out occlusion of the Li coexist is used for negative-electrode material, unlike a clad plate, expansion contraction of the phase which can carry out occlusion of the Li in the case of charge and discharge can be eased, and, moreover, structure can be maintained at stability. Moreover, the alloy of the phase which does not carry out occlusion of the Li which consists of a metallic element belonging to 4A, 5A, and 6A group, and Mn, Fe, Co, nickel and Cu is sufficient also as these metal simple substances again. When Cu and Si were compound-ized as mentioned above, it has improved and the charge-and-discharge property was able to be raised.

[0016] Even if it compound-izes a Cu-nickel alloy and Si like this, a charge-and-discharge property is improvable like the complex of Cu and Si. Therefore, the phase which does not carry out occlusion of the Li must be a phase which consists of 4A, 5A, a 6A group element, and at least one kind of element of Mn, Fe, Co, nickel, and Cu. When the stability in the inside of the electrolytic solution is especially taken into consideration, the alloy which uses Cr, Fe, Co, nickel, Cu(s), and these elements as a main configuration element is desirable.

[0017] As for the particle size, it is [the particle with which the phase which can carry out occlusion of the Li, and the phase which does not carry out occlusion of the Li coexist] desirable that it is 100 micrometers or less. Especially 40 micrometers or less are desirable from the spreading nature and the charge-and-discharge property when producing the negative electrode for Li cells especially.

[0018] The phase which can carry out occlusion of the Li, and the phase which does not carry out occlusion of the Li have the desirable condition of being mixed in respect of stress relaxation as minutely as mutual possible. Capacity is held with a comparatively large value by this at stability, and a cycle life becomes long.

[0019] When producing a negative electrode using the particle with which the phase which can carry out occlusion of the above Li(s), and the phase which does not carry out occlusion of the Li coexist, since the conductivity of the particle itself is good, it is not necessary to use electric conduction material but, and in order to compensate the conductive fall accompanying charge and discharge, electric conduction material can be mixed and a negative electrode can also be formed. If the electric conduction material at this time has good conductivity and its reactivity with the electrolytic solution is weak even if carbon powder also uses metal powder, there will be especially no problem.

[0020] Moreover, a binder is used when producing a negative electrode. As a binder, especially if it does not react, for example with the electrolytic solutions, such as EPDM, PVDF, and polytetrafluoroethylene, it will not be limited. 1-30wt.%, especially 4 - 15% of the loadings of a binder are desirable to the sum total weight of the above-mentioned negative-electrode active material and electric conduction material. It is possible to carry out restoration etc. on the metallic foil of the shape of the shape of a sheet and a film at spreading or a foam metal, and to consider as the negative electrode corresponding to a cell configuration as a negative-electrode configuration using said mixture.

[0021] Thus, the obtained negative electrode can be used as the optimal lithium secondary battery by combining with the positive electrode, the separator, and the electrolytic solution which are usually used. as the active material used for a positive electrode -- LiCoO₂, LiNiO₂, and LiMnO₄ etc. -- the multiple oxide containing a lithium can use, what mixed electric conduction material and a binder to this is applied to charge collectors, such as aluminum foil, and it considers as a positive electrode. As a separator, the porous membrane of polypropylene, polyethylene, or a polyolefine system is used. Moreover, as the electrolytic solution, two or more kinds of mixed solvents, such as propylene carbonate (PC), ethylene carbonate (EC), 1, 2-dimethoxyethane (DME), dimethyl carbonate (DMC), and methylethyl carbonate

(MEC), are used. moreover -- as an electrolyte -- LiPF₆, LiBF₄, and LiClO₄ etc. -- it is and what was dissolved in the above-mentioned solvent is used.

[0022] Increase of charge-and-discharge capacity, improvement in electrical conductivity, improvement in power density, the improvement in a cycle property, and high-speed charge and discharge became possible by using the particle with which the phase which can carry out occlusion of the lithium to the negative-electrode ingredient for lithium secondary batteries, and the phase which does not carry out occlusion of the lithium coexist as a negative-electrode active material.

[0023]

[Embodiment of the Invention]

(Example 1) Si particle with a mean particle diameter of 5 micrometers and Cu particle with a mean particle diameter of 5 micrometers were mixed by V mixer. The mixed weight ratio was set to Si:Cu=1:1. A part of this mixed powder was kneaded with a graphite, amorphous carbon, and N-methyl pyrrolidone solution of PVDF, and it was applied to Cu foil. a mixture -- the weight ratio of each inner component is Si-Cu mixed powder:TJSP:AB:PVDF=85:6:3:6. Moreover, the thickness of Cu foil is 20 micrometers. It is made to dry at 80 degrees C after spreading for several hours, and is 0.5 ton/cm². After pressing by the pressure, the vacuum drying was carried out at 120 more degrees C for 3 hours.

[0024] The negative-electrode sheet was produced by such actuation. The remainder of the above-mentioned mixed powder is 1.0 ton/cm² with the fixture made from Mo. After carrying out press forming by the pressure, every fixture 900 degrees C, and vacuum heating of 1 hour were performed. The acquired Plastic solid was pulverized and Si-Cu joint powder was obtained. Si particle and Cu particle were joined, Si-Cu joint powder formed one particle, and the compound layer of Si-Cu was formed in the interface of Si and Cu. Si-Cu joint powder classified using the screen, and used only powder 32 micrometers or less as negative-electrode material.

[0025] This Si-Cu joint powder was applied to Cu foil by the same combination and same approach as Si-Cu mixed powder, and was processed into the negative-electrode sheet. Unipolar evaluation was carried out having used the counter electrode and the reference pole as Li metal for these negative-electrode sheets. At this time, the electrolytic solution used the solution of EC:DMC=1:2 which contain LiPF₆ 1 mol/l. Moreover, a charge and discharge current is 1 mA/cm². It adjusted so that it might become, and the charge and discharge test was performed in the range whose potential of the negative electrode to a reference pole is 0.01 -1V.

[0026] A charge and discharge test result is shown in drawing 1. In Si-Cu mixed powder, initial charge capacity is very as large as 1865 mAh/g. Moreover, initial discharge capacity was a big value compared with the graphite negative electrode in 553 mAh/g. However, a ratio [as opposed to / the irreversible capacity which is the difference of initial charge capacity and initial discharge capacity is 1312 mAh/g, and / the initial charge capacity of irreversible capacity] is 0.76. It became a very big value. On the other hand, Si-Cu joint powder was initial charge capacity 651 mAh/g and initial discharge capacity 523 mAh/g, and irreversible capacity became very small although charge-and-discharge capacity became small compared with mixed powder. Moreover, although the number of cycles which maintains 95% or more of initial discharge capacity was only 1 cycle in mixed powder, they were 26 cycles with joint powder.

[0027] (Example 2) Mechanical alloying processing was performed for an example 1, Si of the same kind, and Cu powder with planet mold ball milling equipment. The powder weight ratio of Si and Cu is about 1:2. At this time, the container and ball made from stainless steel were used. Since the element which constitutes a container and a ball might mix into powder between mechanical alloying, it loaded only with Cu powder into the container first, and operated ball milling equipment. Then, the container was loaded with Si and Cu powder for compound-izing, and mechanical alloying was performed. The powder obtained by mechanical alloying was in the condition in which Si and Cu carried out the laminating to the shape of a layer, and the thickness of the layer of Si and each Cu was 1 micrometer or less. From the obtained mechanical alloying powder, powder 32 more micrometers or less was classified.

[0028] The negative-electrode sheet was produced using this powder on the same compounding ratio and same production conditions as an example 1. the chemical composition of mechanical alloying powder here -- Si -- 39.3% and Cu -- 60.7% it was . Moreover, the Si-Cu mixed powder mixed by V mixer so that the weight ratio of Si and Cu might be set to about 1:2, and the joint powder which combined this mixed powder like the example 1 also produced the negative-electrode sheet on the same compounding ratio as the above, and production conditions. Although unipolar evaluation of the charge-and-discharge property of these negative-electrode sheets was carried out, the condition is the same as an example 1.

[0029] A charge and discharge test result is shown in drawing 2. Although the presentation was almost equal to any powder, compared with mixed powder, the charge-and-discharge property of joint powder improved, and the property of mechanical alloying powder improved further from joint powder.

[0030] (Example 3) Mechanical alloying was performed for aluminum particle with a mean particle diameter of about 10 micrometers and Cu particle with a mean particle diameter of about 5 micrometers with planet mold ball milling equipment like the example 2. The obtained powder had the layer-like organization like Si-Cu mechanical alloying powder. the chemical composition of aluminum-Cu mechanical alloying powder -- aluminum -- 38.8% and Cu -- 61.2% it was . After this mechanical alloying powder also classified in 32 micrometers or less, the negative-electrode sheet was produced by the same approach as an example 1. Moreover, the mixed powder which mixed aluminum and Cu particle also produced the negative-electrode sheet.

[0031] The charge and discharge test as an example 1 also with these same negative-electrode sheets was carried out. The result is shown in drawing 3. From this, the charge-and-discharge property of mechanical alloying powder improved compared with mixed powder.

[0032] (Example 4) Particle size is NiSi₂ 32 micrometers or less. After mixing a particle and Cu particle with a mean particle diameter of about 5 micrometers by V mixer so that it may be set to 1:1 by the weight ratio, the part produced the negative-electrode sheet with mixed powder, and the remainder was used as joint powder with powder-metallurgy processing like the example 1, and produced the negative-electrode sheet. The negative-electrode sheet production approach here is the same as that of an example 1. Moreover, the charge-and-discharge property as well as an example 1 was examined. The result is shown in drawing 4. Mixed powder was 33 cycles with joint powder to the cycle which maintains 95% of initial discharge capacity being 1 cycle.

[0033] (Example 5) The negative-electrode sheet which makes a subject TJSP which is a graphite system ingredient as an example of a comparison was produced. TJSP and N-methyl pyrrolidone solution of PVDF were kneaded and this was applied to Cu foil. Here, the weight ratio of TJSP and PVDF is 90:10. After this, the conventional-type negative-electrode sheet was obtained by the same production approach as an example 1. Moreover, the charge and discharge test of this conventional-type negative-electrode sheet as well as an example 1 was carried out. The result is shown in drawing 5. Although the charge-and-discharge cycle is stable with the negative-electrode sheet which uses TJSP as a negative-electrode active material, since discharge capacity is about 300 mAh/g, compared with the compound-ized negative electrode shown in examples 1-4, capacity is small.

[0034] (Example 6) It is LiCoO₂ to aluminum foil with a thickness of 20 micrometers. The positive electrode 21 which applied to both sides, dried and rolled out the mixture which set an active material, an artificial graphite, and PVDF to 87:9:4 by the weight ratio so that it might become 90 micrometers of one side, The double spread of the mixture which set to 86:8:6 the NiSi₂-Cu joint powder and the artificial graphite which were produced in the example 4 in Cu foil with a thickness of 20 micrometers, and PVDF by the weight ratio is carried out so that it may become with 50 micrometers of one side. The negative electrode 22 dried and rolled out and the separator 23 with a thickness of 25 micrometers of the porosity made from polyethylene were wound as shown in drawing 6, and they were contained with the dimension 18phix65mm cell can outside, and the property was evaluated, using 1MLiPF₆-EC/DMC as the electrolytic solution.

[0035] The test condition was set to charge-and-discharge rate 0.5C, charge termination electrical-potential-difference 4.2V, and discharge-final-voltage 2.5V. Consequently, the energy density of 320 Wh/l was obtained and the engine performance stabilized up to 100 cycle was shown.

[0036]

[Effect of the Invention] By this invention consisting of particles containing both the phase to which the negative-electrode active material which bears the charge and discharge of a negative-electrode ingredient can carry out occlusion of the lithium, and the phase which does not carry out occlusion of the lithium, the mutual structural change accompanying charge and discharge can be eased mutually, collapse of a particle can be controlled, and charge-and-discharge capacity is large, and irreversible capacity is small and can offer a lithium secondary battery with a long charge-and-discharge cycle life.

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